ter, if there be atoms, may be torn from one another and made to take up new and definite relations, so that by synthesis there arise new substances with new properties, perhaps exhibiting structure and capable of performing purposive action of the most striking and at present inexplicable kind; motion, heat, light, electricity, being manifest in certain cases among other phenomena, while there are present no arrangements, conditions or apparatus such as would enable us to develop these independently of the living. Here, then, as it seems to me, will be found the foundation not only of the principles of physiological, pathological and medical science, but of that of the whole living world as distinguished from the lifeless cosmos. Here we must look for the initiation of all the changes characteristic of the living state. Account must also be taken of these peculiarly vital phenomena in discussions concerning consciousness, thought, and will, and the life that has been, is and is to be. And may we not even hope that by further and deeper study of the phenomena of living matter under the new advantages of demonstration which we enjoy, and which are constantly progressing, some further light may be thrown by the increased skill of investigators of vital phenomena even upon the nature and relationship of material atoms in that boundless world of the non-living which ever has been and must be regarded alike by learned and unlearned with wonder and admiration?

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THE MAJOR PREMISE IN PHYSICAL CHEMISTRY.*

CHEMISTRY is essentially an inductive science, mathematics is essentially deductive, while physics holds an intermediate position. Yet in our own science, generalizations are reached from time to time, which serve as major premises for syllogistic reasoning. For example, the proposition that each portion of matter has constant weight is at the basis of our knowledge of chemical equivalents as determined by the balance; the isolation of the metals of the alkalis and alkaline earths led to an insight into the nature of salts in general as metallic compounds; and the 'periodic law,' though not expressed in precise mathematical language, is a most fruitful generalization of generalizations.

Physical chemistry, following the logical methods already so largely adopted in physics, is characterized by a readiness to use the major premise. Instead of making a separate experiment to answer each question of fact, the conclusion may often be reached on theoretical grounds, in the same sense as an engineer may demonstrate the stability of the structure he has designed, or the movements of a newly invented machine. What, then, is the leading major premise in modern chemistry? and what shall be the conditions of fruitfulness?

The doctrine of energy, as based upon thermodynamics, embraces the two laws of conservation and correlation; first, energy (while convertible from one form to another) is constant in amount; second, while work may be wholly converted into heat, only a definite fraction of heat can be converted into work. To specify more clearly, if a quantity of heat, H, is received at temperature T (from absolute zero), and if this is converted into work as far as possible by any ideal process until there remains the quantity H′ at temperature T′, then the simple theorem holds that the two quantities of heat are proportional to the two temperatures; and of course the difference between heat received, and heat remaining (that is, the work) is proportional to the

*Abstract of a paper prepared by request, to introduce the topic of Physical Chemistry, for the American Association for the Advancement of Science. Read Sept. 2d, 1895.

difference in temperature. Or, in algebraic language,

$$H : H' \quad :: T : T'$$
$$H : H-H' :: T : T-T'$$
$$\text{Work}, = H-H' = \frac{T-T'}{T}.H$$

This equation shows what *fraction* of the heat may be converted into work, under the most favorable conditions; namely, the fall in temperature divided by the absolute temperature at which the heat is supplied.

My present purpose is to present this topic in its bare outlines, and with the greatest simplicity possible. Those who wish to follow the deductive reasoning in detail must use the notation of Calculus, in accordance with the following steps. Combining the formula for the total work (as implied in the first law) with that for work derived from change of temperature (the second law) we deduce a differential equation for the work obtained or required in isothermal changes. The change under consideration may involve external work, as when a vapor or gas is generated against atmospheric pressure; or it may be internal work of different kinds, as when the molecules are endowed with increased kinetic energy in volatilizing, or when a compound is decomposed into its constituents, with increased potential energy.

A somewhat difficult but important paper by J. Willard Gibbs* treats of the equilibrium of heterogeneous substances, giving deductions from the two laws of thermodynamics, which in turn become major premises for a host of further deductions; so broad, indeed, are the propositions of Gibbs, that the distinctions between chemistry and physics do not appear; there may be two 'heterogeneous substances' of like chemical nature, as water and its vapor; there may be three chemical bodies, as limestone with the lime and the carbon dioxid obtained by ignition; or there may be several physical mixtures, as solution of water in ether, solution of ether in water, and the mixed vapor resting upon both liquids. Now, a little consideration will show the importance of knowing when equilibrium is established, for this is equivalent to saying that no further action can take place; the solution is saturated, no longer acting upon the salt; or the gas which has been generated under pressure is no longer evolved. When a change takes place spontaneously, as when I drop a stone, or mix sulphuric acid with water, heat is developed from some other form of energy. To reverse the process, work must be done. The conversion of heat into work is limited by natural law; when a given change implies the doing of work, and that work is forbidden by the terms of our major premise, the change is impossible, equilibrium prevails.

'Osmotic pressure' in dilute solutions is analogous to the pressure of gases; the Gay-Lussac-Marriotte law, with slight modification of terms, applies to molecules in the liquid state. If work is required to diminish the volume of a gas by means of pressure, work is likewise required to diminish the volume of a body in dilute solution, whether the solvent be removed by evaporation or by freezing. Boiling point and freezing point of the solvent are changed by the presence of the dissolved body. The agreement of observed facts with theoretical deductions has led to important methods of determining molecular weights, while the apparent discrepancies in the case of electrolytes have proved an important argument for the doctrine that these compounds are dissociated into their ions.

Our Chairman has pointed out the mutual indebtedness of technology and pure

* Trans. Conn. Acad., **3**, 108, 343 (1874–78). See, also, Amer. Jour. Sci. [3] **16**, 441 (1877); **18**, 277 (1878).

science. Manufacturing processes afford many examples of change which are not carried to completion; it is important to know how far the operation can be improved to afford a larger yield, a purer product or less waste. Combustible gases issue from the blast furnaces. There is still a great reducing power in this mixture of carbon monoxid with carbon dioxid. Can it be utilized by enlarging the furnace? Immense furnaces were built in order to secure a larger yield of iron, but the results were disappointing. The law of mass action shows that the equation

$$Fe_2\,O_3+3\,CO=2\,Fe+3\,CO_2$$

is limited by certain conditions of equilibrium, and that the ratio of the two oxids of carbon could not be greatly improved over that already secured in practice. The expense of a technological experiment might have been saved, had the indications of mathematical chemistry been heeded.

What hopeless confusion seems to prevail in our present knowledge of solubilities; yet how important in the separations required for chemical analysis. Here, again, we deal with questions of equilibrium. Will work be done at the expense of heat or not?

There are two special difficulties in the general application of thermodynamical principles; first, the minor premise is often wanting; and, second, the mathematical form of reasoning is often difficult for the best laboratory workers. Among the published data of thermo-chemistry, some have been determined directly, some indirectly; it is often difficult to find the data desired or to judge of their accuracy. A critical compilation of all available thermal data, conveniently arranged for reference, with at least some indication of the probable errors, would be very desirable. Many such data might be computed indirectly from experimental determinations of equilibrium. Many empirical equations have been computed, showing solubility as a function of temperature. Who will trace the correlation among such, and thus add a large chapter to thermo-chemistry? What genius shall discover that form of mathematical function that shall substitute rational for empirical equations with a clear interpretation for each constant required? "But this work is mathematical rather than chemical," you will say. Yes, it is applied mathematics; and mathematicians (not being chemists) are not likely to undertake such a task for us, unless we ask their counsel and aid. Specialization is inevitable; yet by too arbitrary a specialization, we may inadvertently lose the very help we need. Again would I emphasize the fruitfulness which follows a 'cross-fertilization of the sciences.'* Judging from the advances recorded in late years, especially in the '*Zeitschrift für physikalische Chemie*,' it is safe to predict great developments for the rising generation. I heartily echo the sentiment that we need more data; yet great stores of observations upon record have not yet been coördinated and put to use. Ostwald, desiring to know the influence of free iodin upon a reduction process, made three series of determinations (twenty-four in all) from which he concludes that the influence is *not* proportional to the mass. It was no part of his purpose to discover what the law of retardation is; but others might well follow out this clue, using also the data supplied by Meyerhoffer, and supplementing these with further experiments if needed. A glance at the literature of solubilities, and the lack of rational formulas to express broad generalizations, may convince us that a great mine, with abundant ore 'in sight,' is awaiting development; or, rather, that ore has been run through a stamp mill to extract half the gold, while fully half still remains in

* Jour. Amer. Chem. Soc. **15**, 601 (1893).

the tailings, awaiting more perfect methods of treatment.

Much may be learned from the systematic habits of the astronomer, dividing his work among the several observatories in a spirit of helpful coöperation, and assigning the labor of computation to those who are fitted thus to follow the lead of others. What better service can we do for the University student than to set before him some of the problems in mathematical or physical chemistry that require patient toil, and give him the pleasure of assisting in their solution by the use of logarithms and squares? What is more practical than to utilize any service he can render?

In conclusion, I beg leave to suggest the appointment of a joint committee (representing Sections A, B and C of the American Association) to consider the feasibility of striving towards the following ends:

1. The compilation of all reliable data of physical chemistry in convenient form for reference, distinguishing those determined directly from those calculated indirectly.

2. The calculation of empirical formulas, to combine any series of data, when some better form of generalization is not already at hand.

3. The preparation and use of rational formulas, wherever possible, to deduce the natural constants from series of observations, and to express the conditions that may be expected to hold between observations of different kinds.

4. The organization of a band of volunteer compilers and computers from among advanced students, who (with the counsel and aid of their instructors) may assist in the work of compiling data and computing formulas.

☞ While the time did not seem ripe for the appointment of such committee at the late meeting of the A. A. A. S., the writer would be pleased to receive any further suggestions from those interested, regarding the points noted above.

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REMARKS ON SOME RECENT FUNGI EXSICCATI.

IT is still a favorite mode among mycologists to distribute exsiccati, or series of specimens of fungi collected from time to time by various persons and in different localities. In times past these exsiccati have served a very useful end in enabling collectors to acquaint students with any new discoveries, and it has not been unusual to find many new species described in them. Even at the present day this habit prevails to a greater or less extent, and diagnoses of new species frequently occur in these collections. In the writer's mind, however, the custom, although sanctioned by long usage, is reprehensible, especially in those cases in which the species are not also described in some botanical journal. At a period when such journals were few, and when their circulation was limited, the distribution of exsiccati with these new species was justifiable; but now, with the great increase in means of publication and the facilities for illustration, the necessity for this has passed away. It is, indeed, questionable whether such species can be regarded as published in the strict sense of the word. Exsiccati are from their very nature ephemeral. They are easily destroyed by insects and other pests. They have no place on the shelves of the library. They are very limited in their circulation, and their limited numbers and relatively high price practically place them beyond the reach of the majority of students. Only a small number of persons, therefore, have access to them, and they must be sought for in the larger herbaria of the country. The majority of botanists are therefore seldom cognizant of the new species described in